



Ultrasonication-flotation-advanced oxidation tertiary treatment of oil-based drilling cuttings

Qian Xu^a, Liang Ma^b, Linjing Zhang^b, Yichen Zhang^c, Yingfa Song^d,
Shenwen Fang^{a,*}

^a College of Chemistry and Chemical Engineering, Southwest Petroleum University, Sichuan, Chengdu, 610500, China

^b Quality, Health, Safety and Environmental Protection Department of Zhejiang Oilfield Company, Zhejiang, Hangzhou, 310023, China

^c Natural Gas Exploration and Development Division of Zhejiang Oilfield Company, Sichuan, Luzhou, 646400, China

^d Southwest Gas Production Plant of Zhejiang Oilfield Company, Sichuan, Yibin, 645250, China

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ABSTRACT

The treatment of oil-based drilling cuttings (OBDCs) with high oil content is difficult. In this study, a tertiary treatment of ultrasonication–flotation–advanced oxidation for treating OBDCs with a high oil content of 20.10 wt% was proposed for the first time. All stages of the treatment processes were optimised. The recommended parameters for ultrasonication at room temperature were a mass ratio of OBDCs to the degreaser of 1:8, an ultrasonication power of 600 W and treatment time of 30 min. After the ultrasonication treatment, the oil content of the OBDCs decreased from 20.10 wt% to 5.00 wt%. Flotation was performed at room temperature with a mass ratio of OBDCs to the degreaser of 1:10, a stirring speed of 400 rpm, an aeration head aperture of 3 μm and airflow rate of 400 mL/min under N_2 injection for 60 min. After the flotation treatment, the oil content of the OBDCs decreased from 5.00 wt% to 2.01 wt%. Advanced oxidation was performed at room temperature with a mass ratio of OBDCs to water of 1:10, 3.57 wt% sodium persulphate in water, 4.17 wt% ferrous sulphate heptahydrate in water and ultrasonication power of 1000 W for 100 min. Following the advanced oxidation treatment, the oil content of the OBDCs decreased from 2.01 wt% to 0.58 wt%. The results of this study provide a new method and idea for treating OBDCs with high oil content.

1. Introduction

Oil-based drilling fluid has the characteristics of fast drilling, strong ability to stabilise the borehole wall, little impact on the gas reservoir and good effect in preventing hydration and expansion of the shale layer. Given its strong advantages, it has been widely used in shale gas development [1–3]. Although oil-based drilling fluids provide considerable benefits to drilling, they cause serious environmental pollution [4]. During drilling, oil-based drilling fluid is adsorbed onto the surface of drilling cuttings to form solid waste known as oil-based drilling cuttings (OBDCs), which is a hazardous solid waste according to the National Hazardous Waste List (2021 Edition) of China [5]. Petroleum hydrocarbons in OBDCs (mainly derived from the base oil in oil-based drilling fluids) are biologically toxic. Untreated or improperly treated OBDCs can pollute water and soil after discharge and can even threaten human health [6]. Thus, petroleum hydrocarbons must be effectively removed before they are discharged or recycled [7]. At present, the commonly used

* Corresponding author. 8 Xindu Avenue, Xindu District, Chengdu, Sichuan, 610500, China.
E-mail address: 1104680134@qq.com (S. Fang).

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methods for OBDC treatment primarily include thermal desorption, solvent extraction and chemical cleaning [8].

The principle of the thermal desorption method is to heat the petroleum hydrocarbons in OBDCs for gasification into steam and separate them from the cuttings, such that most of the base oil can be recovered and the clean cuttings can be recycled as a resource [9, 10]. OBDCs that are commonly treated through thermal desorption have an oil content of <15 wt% and a water content of >8 wt%. Furthermore, the oil content of OBDCs after thermal desorption treatment can be less than 1 wt% [11]. Although thermal desorption has a short treatment time and yields good results, this technology is complicated, equipment costs are high and generates cuttings with an unpleasant smell [12].

The principle of the solvent extraction methods is to produce base oil with strong solubility in an organic solvent and extract petroleum hydrocarbons after fully mixing OBDCs with the extraction agent. The most commonly used extraction agents include toluene, petroleum ether, *n*-hexane and ethylene glycol [13–15]. The OBDCs that are commonly treated via solvent extraction have an oil content of <15 wt% and a water content of <10 wt%. Generally, the oil content of OBDCs after solvent extraction treatment can be less than 1 wt% [16]. Solvent extraction offers the advantages of easy operation and extractant reusability. However, this technology also has several disadvantages such as high safety risks, limited universal extractant applicability and high costs.

Chemical cleaning methods are primarily divided into conventional chemical cleaning and advanced oxidation. The principle of conventional chemical cleaning method is to use surfactant aqueous solution to fully contact the OBDCs for reducing the interfacial tension between the base oil and water and remove the base oil from the surface of cuttings [17–20]. Surfactant chemical cleaning can be used for treating OBDCs with both water and oil contents (<20 wt%). It can reduce the oil content of OBDCs up to less than 2 wt% [21]. Surfactant chemical cleaning has high efficiency, low cost and toxicity as well as simple operation. However, it produces considerable surfactant-contained wastewater, which is difficult to treat [22]. The principle of the advanced oxidation method is to directly oxidise petroleum hydrocarbons into CO₂ and H₂O using free radicals, such as SO₄^{·-} and ·OH produced via chemical reactions [23–28]. In the literature [29], the OBDCs treated via advanced oxidation contained 15.24 wt% oil, and the oil content was reduced to 7.34 wt% after treatment. Advanced oxidation has a fast reaction rate, strong degradation ability and is environmentally friendly. However, it has low oil removal rate for OBDCs with high oil and water contents.

In our previous study [30], we used a hydrophilic deep eutectic solvent comprising choline chloride, methanol and water to replace the microemulsion phase in Winsor I microemulsion. White oil was mixed with a hydrophilic deep eutectic solvent and configured into a new surfactant-free degreaser. The degreasing mechanism of this degreaser was as follows: hydrophilic deep eutectic solvent weakened the adsorption of base oil, white oil dissolved the desorbed base oil and hydrophilic deep eutectic solvent occupied the surface of the cuttings, preventing the re-adsorption of base oil. Using this degreaser, we reduced the oil content of the OBDCs from 14.57 wt% oil to 1.34 wt%. However, two problems remained in the application of this degreaser: (1) the cleaning effect was poor for OBDCs with high oil content and strong cohesion (oil content >20 wt%) and (2) the oil content remained excessively high after treatment, surpassing the current environmental protection requirements (<1 wt%) in certain areas of Sichuan Province. Thus, in this study, we propose a tertiary treatment of ultrasonication–flotation–advanced oxidation for OBDCs with high oil content. Our proposed method is expected to reduce the oil content of OBDCs to be less than 1 wt%. Ultrasound can destroy the cohesiveness [31,32] of OBDCs with high oil content, providing a basis for the effective reduction of oil content by flotation. Advanced oxidation was used to further reduce the oil content. The ideas and methods in this research are expected to provide a new reference for the treatment of OBDCs with high oil content and strong cohesion.

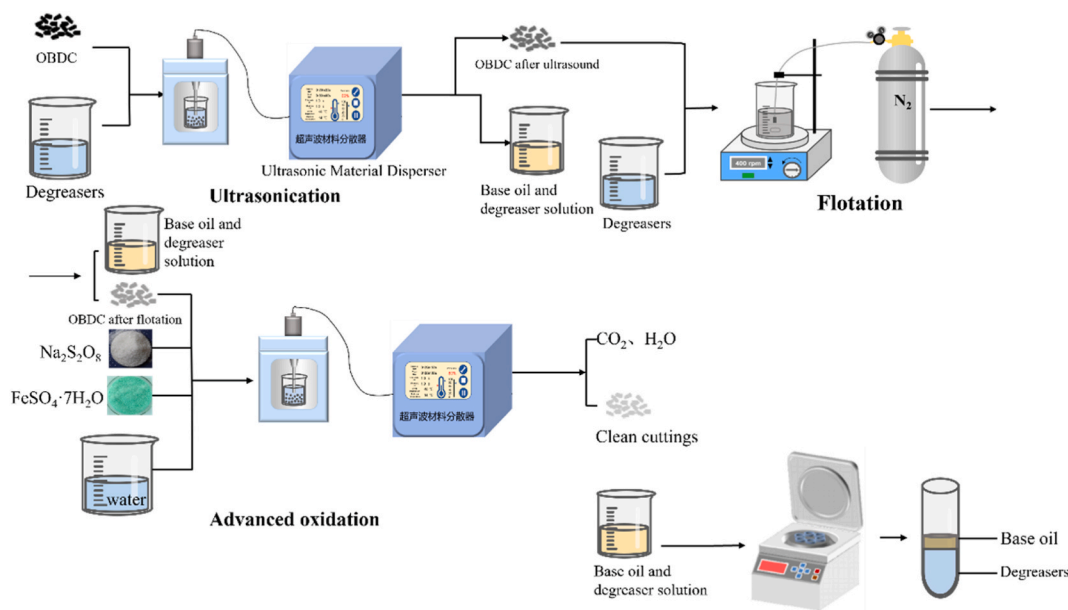


Fig. 1. Schematic of ultrasonication–flotation–advanced oxidation tertiary treatment.

2. Experimental section

2.1. Materials

Ammonium chloride, methanol, sodium persulphate, ferrous sulphate heptahydrate, tetrachloroethylene and *tert*-butanol (TBA) were purchased from Chengdu Kelong Chemicals Company, China. OBDCs were obtained from a shale gas exploitation platform (oil and water content were 20.10 wt% and 21.35 wt%, respectively).

2.2. Ultrasonication–flotation–advanced oxidation tertiary treatment for OBDCs

Fig. 1 shows the schematic of the ultrasonication–flotation–advanced oxidation tertiary treatment process.

2.2.1. Degreaser preparation

NH_4Cl , water and methanol were mixed to configure the degreaser. The mass ratio of methanol to water was 1.48:1, and the mass fraction of NH_4Cl in water was 20 wt%. At room temperature, the three raw materials were added to a beaker. After stirring for 15 min, a transparent homogeneous degreaser was obtained.

2.2.2. Ultrasonication

OBDCs were mixed with the degreaser, and ultrasonication was conducted at room temperature using an ultrasonic material disperser (Nanjing Shunma Instrument Equipment Co., Ltd.). The ultrasonic frequency was 23 kHz and the distance between the ultrasonic probe tip and the liquid–gas interface was 35 mm. In addition, ultrasound was operated in continuous mode.

2.2.3. Flotation

As shown in Fig. 1, first, ultrasonically treated OBDCs were mixed with the degreaser in a 500-mL beaker. Further, the mixture was

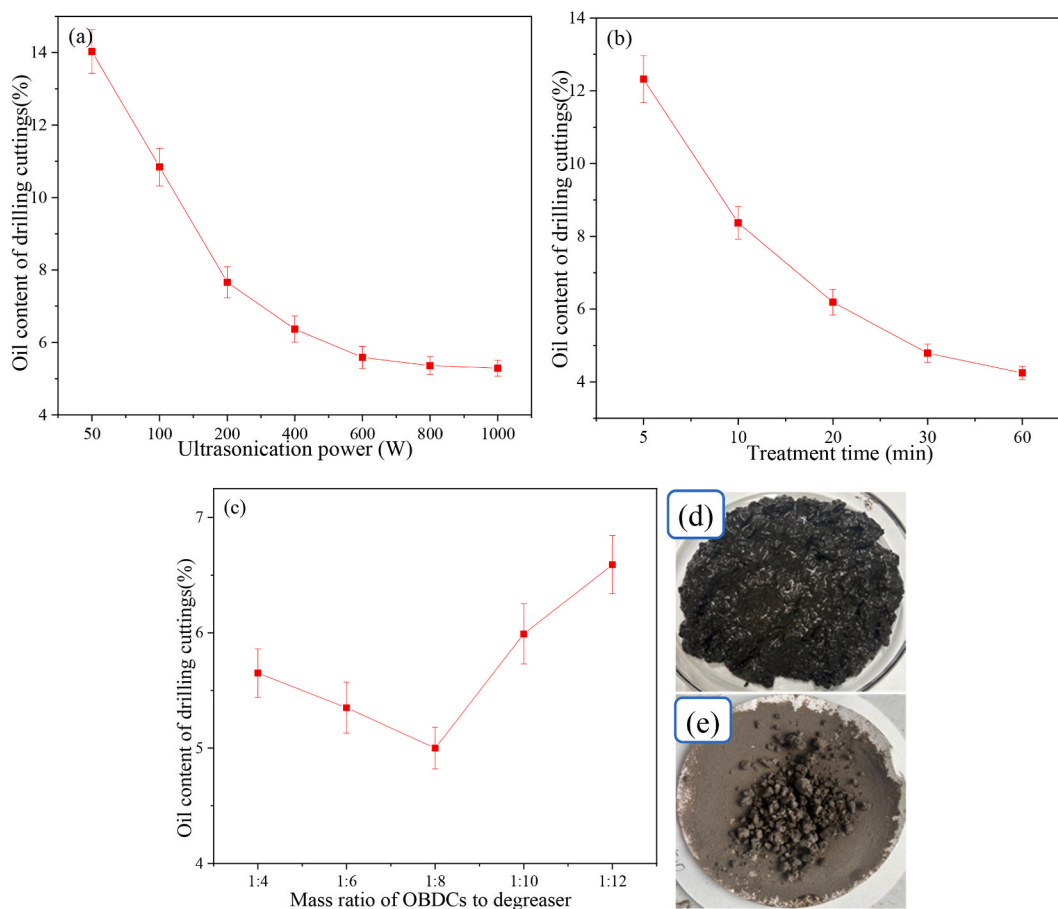


Fig. 2. Effect of (a) ultrasonication power, (b) ultrasonication time, (c) mass ratio of OBDCs to degreaser on the ultrasonication treatment; (d) image of OBDCs before ultrasonication; (e) image of OBDCs after ultrasonication.

magnetically stirred at room temperature. Finally, N_2 was introduced from a porous aerator for flotation.

2.2.4. Advanced oxidation

After flotation, the OBDCs were mixed with an aqueous solution of sodium persulphate and ferrous sulphate and ultrasonicated at room temperature.

In reference to the literature [30], the oil content was measured using a JC-OIL-6 infrared spectrophotometer (Juchuang Environmental Protection Group Co., Ltd., China).

2.3. Measurements

SQI gas chromatography–mass spectrometry (GC–MS, ThermoFisher Company, USA) was used to analyse the base oil components on the surface of OBDCs before and after treatment.

The microscopic morphology and element content on the surface of cuttings before and after treatment were analysed via scanning electron microscopy (SEM) and X-ray energy spectrum analysis (EDS), respectively, and these techniques were conducted on an Inspect F50 instrument (FEI Company, USA).

3. Results and discussion

3.1. Optimisation of ultrasonication and flotation

3.1.1. Optimisation of ultrasonication

The ultrasonic hollowing effect and the degreaser can weaken the adsorption of base oil on the cutting surface. When the OBDCs and degreaser had a mass ratio of 1:8 and were ultrasonically treated at room temperature for 30 min, the effect of ultrasonication power on the treatment was investigated. The results are shown in Fig. 2(a), which illustrates that the oil content of OBDCs decreased to 5.99 wt% at an ultrasonication power of 600 W and decreased negligibly when the power was further increased because both ultrasonication and degreaser had limited treatment effect on oil removal. When the base oil on the surface of the OBDCs was desorbed into the degreaser, the composition of the degreaser was altered and its interfacial activity was influenced, resulting in poor treatment efficacy. As a result, an ultrasonication power of 600 W was recommended for primary treatment.

When the mass ratio of OBDC to degreaser was 1:8 and the ultrasonication power was 600 W, the influence of ultrasonication time on the treatment was investigated, and the results are shown in Fig. 2(b). The results illustrated that as the ultrasonication time increased, the oil content of the OBDCs considerably decreased. When the ultrasonication time was 30 min, the oil content of the OBDCs was 4.79 wt%. When the ultrasonication time was 60 min, the oil content of the OBDCs was 4.25 wt%, with a decrease of only 0.54 wt%. When the treatment time reached a certain value, the cuttings were fully treated and a further increase in treatment time did not increase the treatment efficacy. Thus, an ultrasonication time of 30 min was recommended for primary treatment.

When the treatment was performed with an ultrasonication power of 600 W at room temperature for 30 min, the effect of the mass ratio of OBDCs to degreaser on the treatment was investigated. The results are shown in Fig. 2(c). When the mass ratio of OBDC to degreaser was 1:8, the oil content of OBDC after ultrasonication reached a minimum of 5.00 wt%. This occurred because when the mass ratio was 1:4, too many OBDCs did not come into full contact with the degreaser, resulting in ineffective treatment. When the degreaser was increased, the OBDCs could be fully in contact with the degreaser and the result of the ultrasonication treatment was improved. During ultrasonication, a cavitation effect occurs. Cavitation is the process of forming a gas or vapour chamber within a liquid by lowering the pressure at a constant liquid temperature [33,34]. During cavitation, small bubbles expand rapidly, often

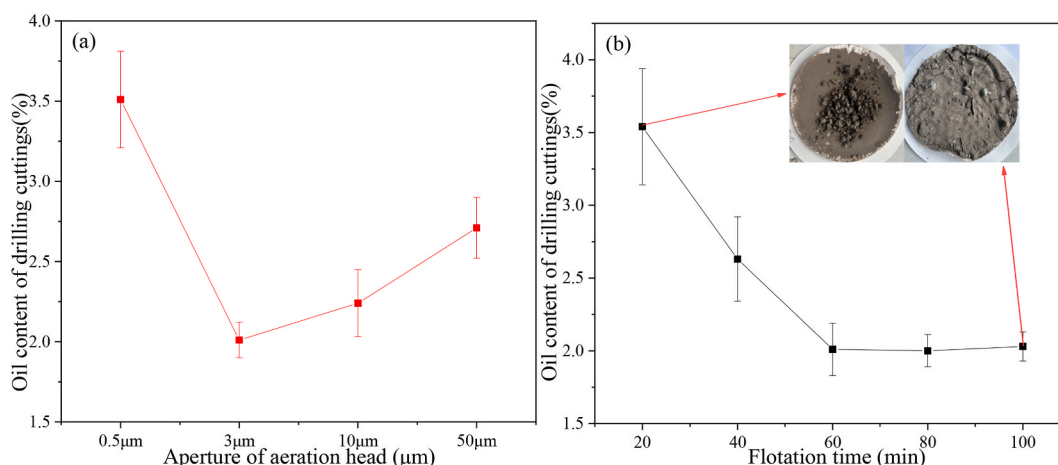


Fig. 3. Effect of (a) aperture of aeration head and (b) flotation time on flotation result.

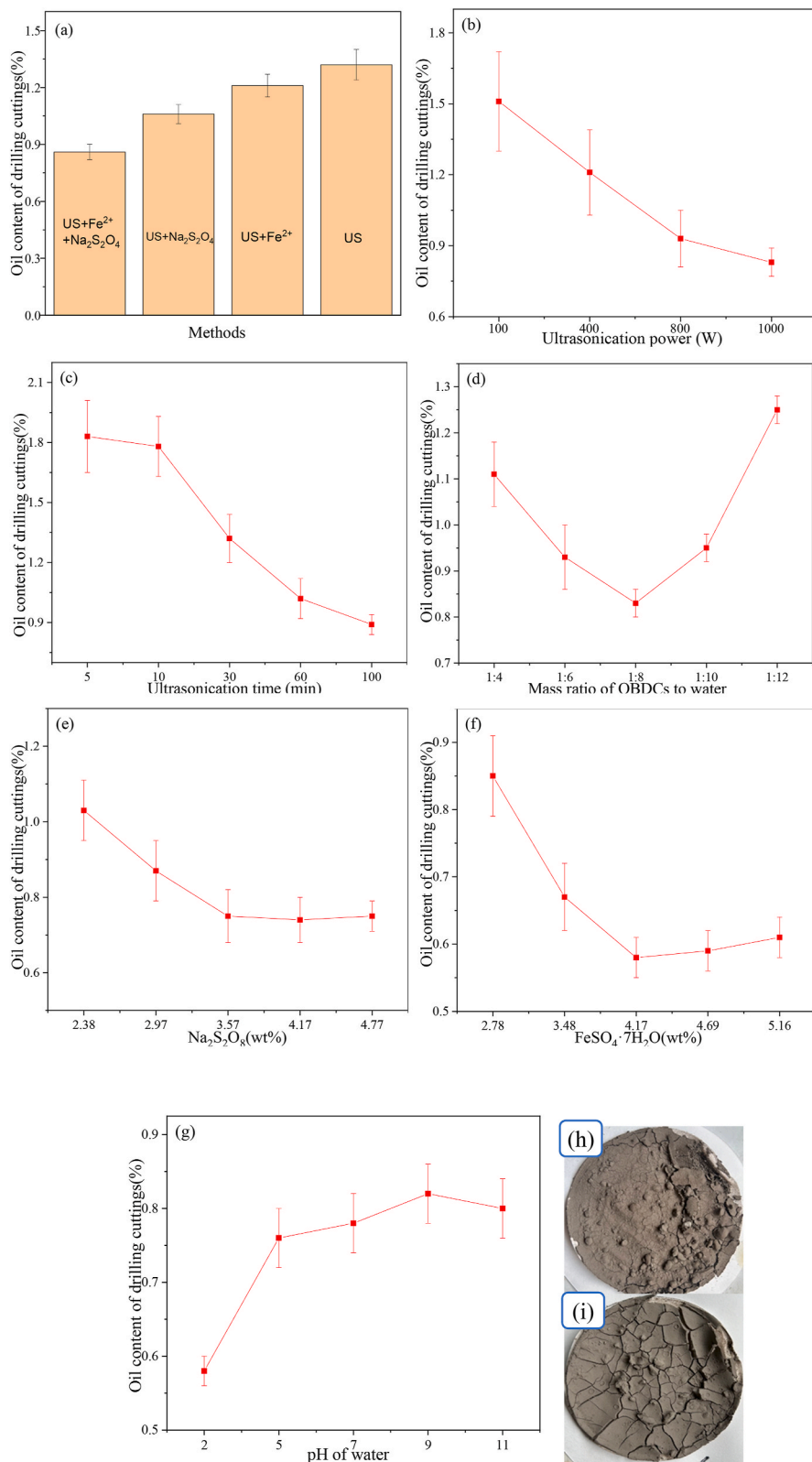


Fig. 4. Effect of (a) advanced oxidation method, (b) ultrasonication power, (c) ultrasonication time, (d) mass ratio of OBDC to water, (e) mass fraction of Na₂S₂O₈, (f) mass fraction of FeSO₄·7H₂O and (g) pH on advanced oxidation treatment results. (h) Image of OBDC before advanced oxidation. (i) Image of OBDC after advanced oxidation.

reaching many times their original size and then violently collapse during the positive pressure half-cycle, splitting into numerous smaller bubbles. When there was too much degreaser, the cuttings in the degreaser were too dispersed, and the air bubbles generated by the cavitation effect could not fully contact the base oil on the surface of the cuttings, thereby worsening the treatment [35]. Thus, a mass ratio of OBDC to degreaser of 1:8 was recommended for primary treatment.

Based on the above results, the recommended process conditions for primary treatment were a mass ratio of OBDC to degreaser of 1:8, an ultrasonication power of 600 W and 30 min of treatment at room temperature. After pre-treatment, the oil content of the OBDCs decreased from 20.10 wt% to 5.00 wt%. The images of OBDCs before and after treatment under the above conditions are shown in Fig. 2(d) and (e), respectively.

3.1.2. Optimisation of flotation

The flotation samples were OBDCs after ultrasonication treatment, with an oil content of 5.00 wt%. The influence of the aperture of the aeration head on flotation treatment was investigated under the following conditions: mass ratio of OBDCs to degreaser of 1:10, stirring speed of 400 rpm, N_2 gas flow rate of 400 mL/min and 60 min of treatment at room temperature. The results (Fig. 3(a)) reveal that when the aperture of the aeration head was 0.5 μm , the oil removal of flotation was the worst, with a decrease in oil content of only 3.51 % because the small particles in the OBDCs easily caused blockage of the aeration head, resulting in poor oil removal. However, when the apertures of the aeration head were 10 μm and 50 μm , the air bubbles were considerably large, resulting in poor contact with cuttings and poor flotation. When the aperture of the aeration head was 3 μm , the blockage of the aeration head did not occur, the bubbles had appropriate sizes to contact the cuttings and the flotation result was improved. Thus, the aperture of the aeration head was selected as 3 μm .

The influence of flotation time on the flotation result was investigated at room temperature with a mass ratio of OBDCs to degreaser of 1:10, stirring speed of 400 rpm and N_2 gas flow rate of 400 mL/min. The results (Fig. 3(b)) revealed that the oil content of the OBDCs rapidly decreased within 60 min and tended to stabilise after 60 min. With increasing flotation time, the desorption of base oil on the surface of cuttings gradually increased. When the flotation time reached a certain duration, the cuttings were fully processed and treatment efficacy did not improve even with an increase in flotation time. Thus, the optimal flotation time was selected as 60 min.

In summary, the optimal flotation conditions are as follows: room temperature, mass ratio of OBDC to degreaser of 1:10, stirring speed of 400 rpm, aeration head of 3 μm and airflow rate of 400 mL/min. The oil content of the OBDCs reduced from 5.00 wt% to 2.01 wt%.

3.2. Process optimisation for advanced oxidation

3.2.1. Process optimisation

The samples of advanced oxidation treatment were OBDCs after flotation treatment and the initial oil content was 2.01 wt%. When advanced oxidation was performed at room temperature for 100 min with a mass ratio of cuttings to water of 1:8 and ultrasonication power of 1000 W, the effects of the advanced oxidation method on the treatment were investigated, and the results are shown in Fig. 4 (a). The treatment result of $\text{Na}_2\text{S}_2\text{O}_8 + \text{Fe}^{2+} + \text{US}$ was much better than the others. After treatment with $\text{Na}_2\text{S}_2\text{O}_8 + \text{Fe}^{2+} + \text{US}$, the oil content of the OBDCs was reduced to 0.86 wt%. Thus, the best approach to activate $\text{Na}_2\text{S}_2\text{O}_8$ was the synergistic activation of ultrasonic and ferrous iron.

When the mass ratio of cuttings to water was 1:8 and both mass fractions of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water were 2 wt%, ultrasonication was performed at room temperature for 60 min to investigate the effect of ultrasonication power on the treatment result, and the results are presented in Fig. 4(b). With the increase in ultrasonication power, the oil content considerably decreased. When the ultrasonication power was 1000 W, the oil content was reduced to 0.83 wt%. The cavitation effect caused by ultrasonication increased with increasing ultrasonication power. The local temperature increase caused by cavitation bubble collapse strengthened the activation of $\text{Na}_2\text{S}_2\text{O}_8$, generated additional free radicals, improved the oxidation efficiency and reduced the oil content.

When the mass ratio of cuttings to water was 1:8, both mass fractions of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water were 2 wt% and the ultrasonication power was 1000 W; the effect of ultrasonication time on the treatment result was investigated at room temperature, and the results are depicted in Fig. 4(c). With increasing ultrasonication time, the oil content gradually decreased, and the lowest oil content was 0.89 wt% when the treatment time was 100 min. The longer the treatment time, the more free radicals would be produced and the better treatment would be. When the treatment time was 100 min, $\text{Na}_2\text{S}_2\text{O}_8$ gradually reacted completely and the efficacy did not increase with a further increase in treatment time. Thus, the optimal treatment time was 100 min.

When both the mass fractions of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were 2 wt% and the ultrasonication power was 1000 W, the effect of the mass ratio of cuttings to water on the treatment result was investigated, and the results are shown in Fig. 4(d). With the increasing mass ratio of OBDCs to water, the oil content first decreased and then increased. When the mass ratio of OBDCs to water was 1:8, the minimum oil content was 0.83 wt%. When the water content was relatively small, the reaction system was in a mud state, some of the OBDCs formed clusters and the OBDCs could not mix well with $\text{Na}_2\text{S}_2\text{O}_8$ solution. The degree of contact between OBDCs and water influences the oxidation efficiency. When the water content increased, the dispersion of OBDCs in water increased and the free radicals generated by $\text{Na}_2\text{S}_2\text{O}_8$ were more likely to react with the pollutants on the surface of the OBDCs. In the presence of excess water, the mass fraction of $\text{Na}_2\text{S}_2\text{O}_8$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and free radicals as well as the oxidation efficiency decreased, thereby increasing the oil content. Thus, the optimal mass ratio of OBDCs to water was 1:8.

When the mass ratio of cuttings to water was 1:8 and the mass fraction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was 2 wt%, the influence of $\text{Na}_2\text{S}_2\text{O}_8$ mass fraction on the treatment result was investigated, and the results are shown in Fig. 4(e). When the mass fraction of $\text{Na}_2\text{S}_2\text{O}_8$ was more than 3.57 wt%, the oil content was approximately 0.75 %. When the amount of $\text{Na}_2\text{S}_2\text{O}_8$ reached a certain value, further addition of

$\text{Na}_2\text{S}_2\text{O}_8$ did not improve the treatment. Studies have revealed that when the oxidant is not present in excess, the generation of $\text{SO}_4^{\cdot-}$ increased with the increasing $\text{Na}_2\text{S}_2\text{O}_8$ mass fraction and the treatment improves [36]. When the oxidant was present in excess, the excess $\text{Na}_2\text{S}_2\text{O}_8$ instantly generated considerable free radicals that quenched each other such that the treatment result could not be further improved. Thus, the optimal amount of $\text{Na}_2\text{S}_2\text{O}_8$ was 3.57 wt%.

When the mass ratio of cuttings to water was 1:8, the mass fraction of $\text{Na}_2\text{S}_2\text{O}_8$ was 3.57 wt%, the influence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ mass fraction on the treatment result was investigated and the results are depicted in Fig. 4(f). As the mass fraction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ increased, the generation of free radicals by $\text{Na}_2\text{S}_2\text{O}_8$ increased, thereby reducing the oil content. Studies have revealed that high Fe^{2+} concentration was not conducive to advanced oxidation. Excess Fe^{2+} would react with $\text{SO}_4^{\cdot-}$, thereby reducing oxidation efficiency [37]. When the mass fraction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ increased to 5.16 wt%, the oil content increased, indicating that the amount of Fe^{2+} was excessive. Thus, the optimal mass fraction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was 4.17 wt%.

When the mass ratio of cuttings to water was 1:8 and the mass fractions of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were 3.57 wt% and 4.17 wt%, respectively; hydrochloric acid and sodium hydroxide were added to adjust the pH. The effect of pH on the treatment result was investigated, and the results are shown in Fig. 4(g). When the pH was 2, the minimum oil content of the OBDCs was 0.58 wt%. After the pH was increased to 5, the oil content of the OBDCs remained almost unchanged because Fe^{2+} was easy to precipitate. When the pH was greater than 5, the precipitation of Fe^{2+} was completed. During this period, Fe^{2+} had no activation effect on $\text{Na}_2\text{S}_2\text{O}_8$ and only ultrasound exhibited an activation effect. Furthermore, the oil content remained unchanged. When the pH was 2, numerous Fe^{2+} were present. During this period, the activation effect on persulphate was the best and the oil content was the lowest.

In summary, the recommended advanced oxidation process conditions are as follows: mass ratio of cuttings to water of 1:8, $\text{Na}_2\text{S}_2\text{O}_8$ of 3.57 wt%, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ of 4.17 wt%, pH of 2, ultrasonication power of 1000 W and room temperature. After 100 min of treatment, the oil content decreased from 2.01 wt% to 0.58 wt%. Images of OBDCs before and after treatment under these conditions are shown in Fig. 4(h) and (i), respectively.

In addition, the advantages and disadvantages of different methods are summarised in Table 1.

The untreated and advanced-oxidation-treated cuttings were observed using SEM. Fig. 5 (a) and Fig. 5 (b) show images of cuttings before treatment, which were irregular and easily agglomerated with each other in the presence of base oil. Fig. 5(c) and (d) show images of cuttings after treatment. The particle size distribution of the cuttings broadened and numerous small cuttings were present. The cuttings were dispersed and did not agglomerate with each other, indirectly indicating that the base oil on the surface of the cuttings had been removed.

EDS was performed and the detection results are presented in Table 2. Further, the C content of cuttings was considerably reduced after treatment, indicating that most of the base oil had been removed and that the tertiary treatment had a good effect.

3.2.2. Process analysis

In this study, ferrous ions and ultrasound synergistically activated sodium persulphate were used for the treatment of organic pollutants in OBDCs. The free radicals generated by activated sodium persulphate are expected to directly oxidise the base oil on the surface of OBDCs into CO_2 and H_2O . Sodium persulphate can produce $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, which can oxidise the base oil. Methanol contains $\alpha\text{-H}$, which is the quencher of $\text{SO}_4^{\cdot-}$ given its high quenching rate constant. TBA lacks $\alpha\text{-H}$, which can react strongly with hydroxyl radicals and slowly with sulphate radicals. Thus, TBA is a quencher of hydroxyl radicals [38]. The oil content obtained when sufficient amounts of methanol and TBA were added as quenchers during the treatment was analysed. Thus, the reaction mechanism of $\text{US} + \text{Fe}^{2+} + \text{Na}_2\text{S}_2\text{O}_8$ advanced oxidation was inferred.

The results shown in Fig. 6 reveal that when a sufficient amount of methanol was added as an $\text{SO}_4^{\cdot-}$ quencher, $\text{SO}_4^{\cdot-}$ had no activation. During this time, the oil content decreased to 0.90 wt%. When a sufficient amount of TBA was added, $\cdot\text{OH}$ was quenched, $\text{SO}_4^{\cdot-}$ was not quenched and the oil content of OBDCs decreased to 0.68 wt%. Thus, $\text{SO}_4^{\cdot-}$ was primarily oxidised followed by $\cdot\text{OH}$ in the oxidation treatment of OBDCs by $\text{US} + \text{Fe}^{2+} + \text{Na}_2\text{S}_2\text{O}_8$.

The base oil on the cutting surface before and after treatment was detected using GC-MS, and the results are provided in Table 3. Following the tertiary treatment, there was a considerable reduction in the petroleum hydrocarbon content in the base oil on the surface of the cuttings. Most petroleum hydrocarbons were removed, leaving only a small amount that had oxidised into alcohols and

Table 1
Advantages and disadvantages of different methods.

Method	Advantages	Treatment samples	Disadvantages
Thermal desorption	The treatment time is short and the oil content can be less than 1 % after treatment.	Oil content of <15 wt% and water content of >8 wt%.	Equipment cost is high and the treated cuttings generate an unpleasant smell.
Solvent extraction	Easy operation; extractant reutilisation capability; oil content less than 1 % after treatment.	Oil content of <15 wt% and water content of <10 wt%.	High safety risks, limited universal extractant applicability and high costs.
Chemical cleaning	High efficiency, low cost and toxicity as well as simple operation. The oil content can be less than 2 % after treatment.	Both water and oil contents of <20 wt%.	Surfactant-contained wastewater was produced; the surfactant and base oil cannot be reused.
Ultrasonication-flotation-advanced oxidation	It can be operated at room temperature and is safe. It is suitable for the treatment of OBDCs with high oil content.	Both water and oil contents of >20 wt%.	The treatment time is long and the process is relatively complex.

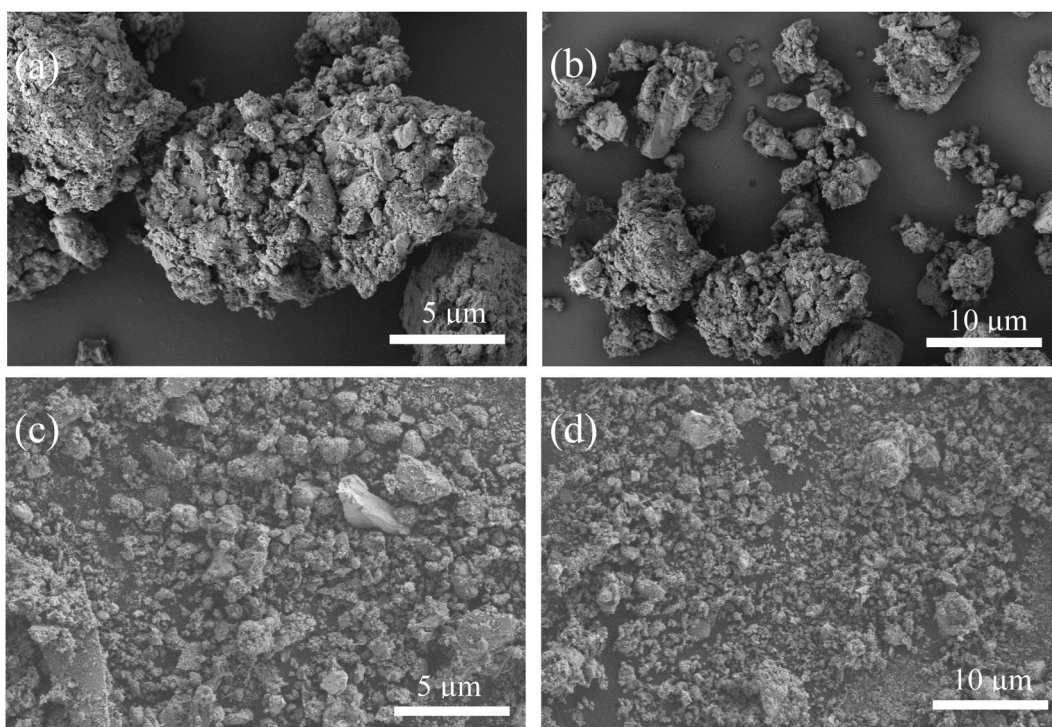


Fig. 5. (a) and (b) SEM images of cuttings before treatment; (c) and (d) SEM images of cuttings after tertiary treatment.

Table 2

EDS detection results of cuttings.

Element (wt.%)	C	O	Ba	Mg	Ca	S
Before treatment	30.83	28.56	28.09	0.07	0.60	10.39
After treatment	3.02	36.87	42.67	0.52	2.30	12.28

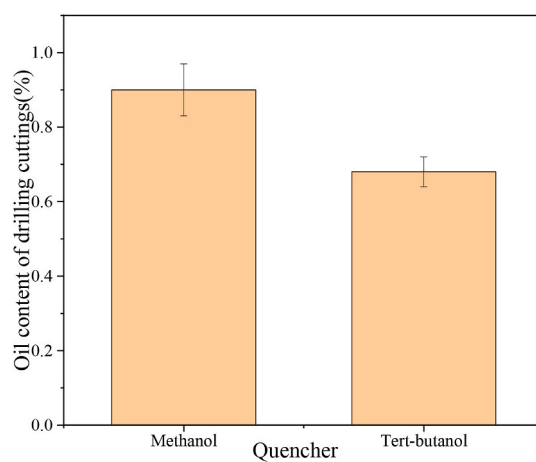


Fig. 6. Effect of different quenchers on the oil content of OBDCs.

Table 3

GC–MS results of the base oil on the surface of cuttings before and after tertiary treatment.

Before treatment	C ₁₅ H ₃₂	C ₂₁ H ₄₄	C ₁₉ H ₄₀	C ₁₆ H ₃₄	C ₁₈ H ₃₈	C ₂₀ H ₄₂
Content (%)	30.27	29.33	15.73	7.31	5.77	4.48
After treatment	C ₈ H ₁₆ O	C ₈ H ₁₈ O ₂	C ₈ H ₁₈ O ₃	C ₁₁ H ₂₂ O ₂	C ₃ H ₆ S	C ₄ H ₈ O ₃
Content (%)	29.8	17.90	16.20	12.30	11.70	8.80

ethers, which remained within the cuttings. Therefore, the proposed tertiary treatment method had an obvious oxidative effect.

4. Conclusion

A tertiary treatment process of ultrasonication–flotation–advanced oxidation for treating OBDCs with a high oil content of 20.10 wt % and strong cohesion was proposed for the first time, and the conditions of each treatment stage were optimised. The ultrasonication conditions were as follows: ultrasonication power of 600 W, mass ratio of OBDC to degreaser of 1:8 and 30 min of treatment at room temperature. The oil content of OBDC decreased from 20.10 wt% to 5.00 wt% after primary treatment under the above conditions. The optimal flotation conditions were as follows: mass ratio of OBDCs to degreaser of 1:10, stirring speed of 400 rpm, aeration head size of 3 μm, airflow rate of 400 mL/min, N₂ injection for 60 min at room temperature. Under these conditions, the oil content of OBDCs reduced from 5.00 wt% to 2.01 wt%. The advanced oxidation conditions were as follows: mass ratio of OBDCs to water of 1:8, mass fraction of sodium persulphate of 3.57 wt%, mass fraction of ferrous sulphate heptahydrate of 4.17 wt%, ultrasonication power of 1000 W and pH of 2. The oil content of OBDCs reduced from 2.01 wt% to 0.58 wt% after 100 min of treatment under these conditions at room temperature.

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Data availability statement

Data will be made available on request.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Qian Xu: Writing – original draft, Formal analysis, Data curation. **Liang Ma:** Funding acquisition, Conceptualization. **Linjing Zhang:** Resources. **Yichen Zhang:** Validation. **Yingfa Song:** Validation, Conceptualization. **Shenwen Fang:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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